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EFFECT OF THE REVERSIBILITY OF BAO OXIDATION DURING WELDING OF ELECTROVACUUM GLASS

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It is shown that the formation of bands of gas bubbles in a weld seam is due to reversible oxidation of barium oxide in the temperature interval 300 – 600°C. To prevent negative consequences of this process when welding a glass bulb and cylinder for introducing electronics, the bulb glass must be heated rapidly up to temperature 700 – 730°C and welding must be performed at a temperature above the upper oxidation temperature of barium oxide.

In the production of kinescopes, glass defects which are often encountered consist of bands of secondary bubbles in the weld seam of the bulb welded with a cylinder for introducing electronics. High internal stresses always arise in the weld zone because of the difference of the chemical compositions and the CLTE of the glasses; these stresses are not completely removed, even by annealing. For this reason, defects in the zone of glass with a high concentration of internal stresses, such as gas bubbles or opaque insoluble inclusions, decrease even more the mechanical and thermal mechanical strength of a seam. In subsequent technological assembly operations, the glass cylinders often separate from the bulb, increasing the number of rejections and the cost of the product.

The purpose of the present investigations is to determine the reasons for the formation of secondary glass bubbles in the weld seam between the glass bulbs and cylinders and to develop a method for eliminating this defect.

An FMP-951/3000 optical pyrometer was used to measure the temperature of the glasses being welded. The structure and texture of the bands of glass bubbles in a weld seam were investigated using an OLYMPUS CX3ILBSF optical microscope. Photographs were made with an attachment to an OLYMPUS C-5050Z camera with total magnification $\times$ 40 and $\times$ 100.

The chemical compositions of the welded glasses of the cylinders and bulbs of kinescopes are presented in Table 1. Evidently, the bulb glass contains about 2.3% BaO and barium oxide is completely absent from the glass used for the cylinders.

The formation of secondary gas bubbles during welding of the glasses was investigated first using the generally accepted technological parameters.

The bulb and cylinder glasses are welded on 10-position automated carousel welding stand. The glass parts being welded are heated simultaneously at the fourth and fifth positions using flame burners in which a mixture of natural gas with oxygen is burned. The burners are located above the arc. For uniform heating of the edges of the articles being welded together the articles are constantly rotating around their axes. The residence time of individual sections in the flame zone is not the same, and therefore the temperatures to which the edges of the articles are heated are different. The nonuniformity of the heating also increases because of the difference of the thermal conductivity of glasses with different chemical composition and different thickness of the walls

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TABLE 1.

Glass	Mass content,%									
	SiO_2	Al_2O_3	Na_2O	K_2O	BaO	PbO	MgO	CaO	Sb_2O_3	Fe_2O_3
Bulbs	58.5 ± 1.00	3.5 ± 0.30	6.7 ± 0.50	8.7 ± 0.50	2.3 ± 0.30	13.0 ± 1.00	2.3 ± 0.50	5.0 ± 0.50	< 0.35	< 0.35
Cylinders	55.0	2.0	3.8	9.2	–	30.0	–	–	–	–

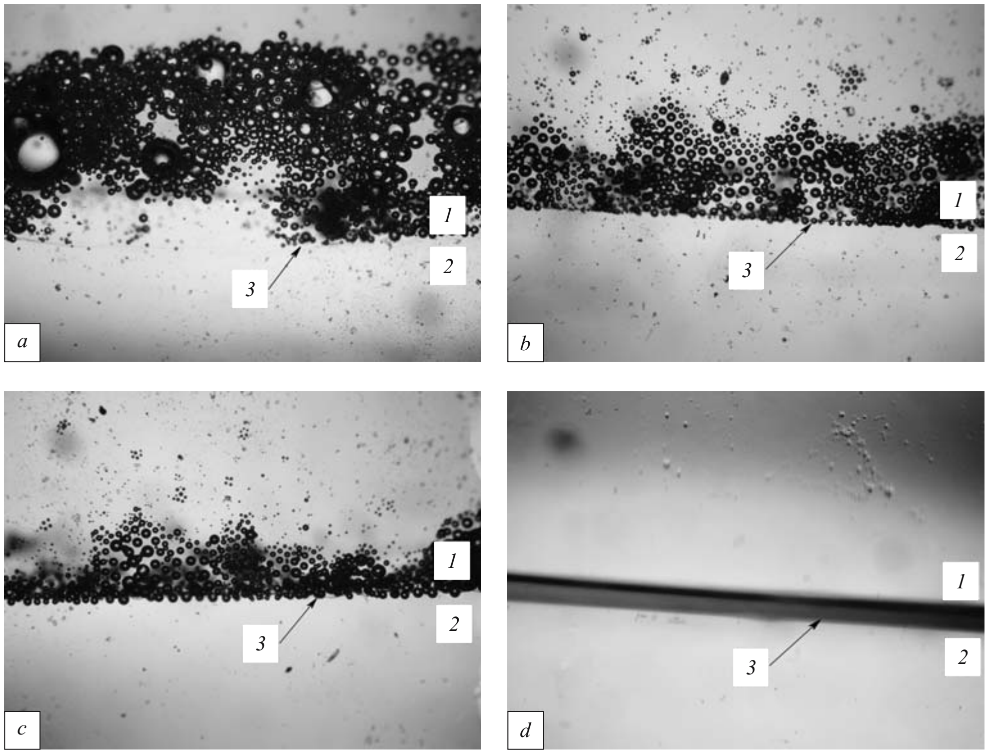

Fig. 1. Structures and textures of characteristic sections of a band of bubbles in a weld seam (× 40): *a*, *b*, *c*) sections with different weld band width at the welding temperatures used for production; *d*) weld band with no bubbles with glasses heated above the oxidation temperature of BaO; *1*) bulb glass; *2*) cylinder glass; *3*) welding seam.

being welded (3.3 and 2.5 mm for the bulb and cylinder, respectively).

The temperature measurements performed with an optical pyrometer established that before joining in the sixth position the bulb glass is heated up to 530 – 550°C and the cylinder glass is heated up to 780°C. To smooth the welding surface, the temperature of the seam is increased up to 850 – 900°C with a sharp flame of the burners in the next position. In the 8th position a wide low-temperature flame anneals the welding seam, and in the 9th and 10th positions the seam cools under natural conditions. After such temperature regimes adopted for glass welding, a band of white light with nonuniform thickness, probably consisting of secondary gas bubbles, can be seen in the seam even with the naked eye.

The structures and textures of the characteristic sections of the band of bubbles in a weld seam are displayed in Fig. 1. It has been determined that bands of gas bubbles appear only in the bulb glass above the interface between the different glasses. This indicates that there is a relation between the appearance of gas bubbles and the chemical composition of the glass — no gas bubbles were seen in the cylinder glass.

Optical analysis of the band of secondary bubbles showed that the width of the band of intense release of bubbles is different and gradually decreases from about 1.5 to 0.5 mm into the bulb glass from the interface of the glasses being welded. The predominating, largest gas bubbles with a quite regular spherical shape about 0.1 mm in diameter form on the widest section of the band. Individual bubbles with diameter exceeding 0.2 mm are also encountered on the same section, and a zone of less concentrated and much smaller bubbles about 0.05 mm in diameter extends beyond the band of large bubbles into the interior region of the glass. In the central and narrowest part of the band of gas bubbles, the bubble size is more uniform and bubbles approximately 0.09 mm in diameter predominate. The character of the variation of the width of the band of secondary gas bubbles in a weld seam and the character of the stepped change in the bubble sizes indicates that there is a relation between the formation of secondary bubbles and the nonuniformity of the heating of individual sections of the bulb glass when this glass is welded to the cylinder glass. It should be noted that no gas bubble formation was observed on any section of the glass used for the cylinder to introduce electronics.

All this shows that the reasons for the appearance of secondary gas bubbles in the weld seam are connected with the presence of BaO in the bulb glass and with the change in the temperature of the bulb glass during welding.

The influence of BaO on the properties of a glass is well-known. However, its exceptional property — to form reversibly barium dioxide which, as temperature increases, decomposes peritecticly back to barium oxide with oxygen

being released [1 – 4] — has a negative effect on the technological operation of welding glass.

Whitherite $BaCO_3$, which is used in electrovacuum glass batch, decomposes less easily and at a higher temperature than alkali-metal carbonates; it releases CO_2 only at temperatures above 1360°C with intermediate formation of the double compound $BaO \cdot BaCO_3$ [5]. The barium oxide which appears when whitherite decomposes differs by its high melting temperature — 1923°C. On the other hand, in the presence of oxygen and with barium oxide heated to comparatively low temperatures (270 – 600°C) it transforms into dioxide:

$$2BaO_2 \rightleftarrows 2BaO + O_2.$$

Investigations of the equilibrium phase states of the system $BaO – BaO_2$ in not only inert gases but also oxygen [1 – 4] have established that the decomposition of barium dioxide is more peritectic than eutectic, and the reversibility of this process appreciably modifies the kinetic parameters of the process. Surface phenomena have a large effect on the formation of nuclei of barium mono-oxide and oxygen diffusion. These processes also appear under production conditions during welding of the glass used for cylinder for introducing electronics with the glass of the kinescope bulb.

The following experiments were performed to determine the reasons for the formation of secondary bubbles in the zone of a weld seam. In the first series of experiments, five experimental bulbs were placed in the carousel machine. The edges of the walls being welded with a sharp flame were heated up to 870°C, at which temperature, with the viscosity and surface tension decreasing, the surface of the walls melted and the melt started to flow spontaneously under gravity. After cooling, no secondary gas bubbles were observed to form in the melting zone in any of the experimental bulbs.

Likewise, after five experimental cylinders for introducing electronics were subjected to the same heat treatment, no secondary gas bubbles were observed to appear during welding.

The results of these experiments have shown that the formation of secondary gas bubbles cannot be related with the release of gases dissolved in the glass melt.

For the second series of experiments, five experimental bulbs and five experimental cylinders were placed in the carousel machine, and the burner collectors were mounted at a height so that the burners heated the edges of the cylinder more than the edges of the bulb. The burn regime in the burners was established so that at the moment the cylinder joined with the bulb in the sixth position the edge of the bulb would be heated up to 520°C and the edge of the cylinder up to 870 – 900°C. The temperature of the bulb glass was chosen so that conditions conducive to oxidation of BaO by the oxygen flow and by oxygen in the air dissolved in the melt would be created. In the seventh position of the carousel machine, a white band of secondary gas bubbles appeared in the weld seam when the temperature reached 790°C. This occurred with all five weld seams in the samples tested.

The following series of experiments was conducted, in a manner so as to prevent the appearance of barium dioxide when the glass articles are heated before they are welded, in order to verify the reason for the formation of secondary gas bubbles — reverse transformation of BaO into BaO_2 and its subsequent decomposition with oxygen being released. To this end, the position of the burners was set so that the edge of the experimental bulbs heated rapidly, before welding, up to 710 – 730°C and the edge of the cylinders up to 840 – 880°C. In this case the welding of all five experimental samples was conducted at a temperature above the maximum temperature for the interval of formation of barium dioxide (270 – 600°C), and a band of gas bubbles did not form either in the position for smoothing the weld seam at a higher temperature or during annealing and cooling of the welded glass parts of kinescopes (see Fig. 1*d*). On cooling, the weld seam unavoidably falls into the temperature interval of the reverse formation of barium dioxide (600 – 270°C), but in order for it to decompose and gas bubbles to be released the temperature must increase up to 790°C, which is impossible during cooling.

It can be concluded on the basis of the results of the present experiments that a band of gas bubbles forms in a weld seam because of reversible oxidation of barium oxide in the temperature interval 300 – 600°C. To prevent negative consequences of this process during welding of the bulb glass and the glass of the cylinder for introducing electronics, the bulb glass must be rapidly heated up to 700 – 730°C and welding must be performed at the maximum oxidation temperature of barium oxide (600°C). Similar processes of reversible oxidation of BaO can also be observed when other types of glasses (technical, art) containing an elevated amount of BaO are welded together.

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